PATENT
ADAA:105

ELECTROCHEMICAL CELL

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NUMBER: RB 710 384 158 US
DATE OF DEPOSIT: MARCH 4, 1994

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THIS INVENTION relates to an electrochemical cell.

According to the invention, there is provided an electrochemical cell, which comprises

as at least part of an anode, a lithium transition metal oxide or sulphide compound which has a $[B_2]X_4^{n-}$ spinel-type framework structure of an $A[B_2]X_4$ spinel wherein A and B are metal cations selected from Li, Ti, V, Mn, Fe and Co, X is oxygen (O) or sulphur (S), and n- refers to the overall charge of the structural unit $[B_2]X_4$ of the framework structure, and the transition metal cation of which in its fully discharged state has a mean oxidation state greater than +3 for Ti, +3 for V, +3,5 for Mn, +2 for Fe and +2 for Co;

as at least part of a cathode, a lithium metal oxide or sulphide compound; and

an electrically insulative lithium containing liquid or polymeric electronically conductive electrolyte between the anode and the cathode, such that, on discharging the cell, lithium ions

are extracted from the spinel-type framework structure of the anode, with the oxidation state of the metal ions of the anode thereby increasing, while a concomitant insertion of lithium ions into the compound of the cathode takes place, with the oxidation state of the metal ions of the cathode decreasing correspondingly.

The compounds of the anode and cathode may, in particular, be lithium metal oxide compounds.

While the cell can be a primary cell, it is envisaged that it may, in particular, be a rechargeable or secondary cell in which the reverse reactions to those set out above, take place during charging of the cell.

Thus, spinel compounds have structures that can be represented by the general formula $A[B_2]X_4$ given hereinbefore, and in which the X atoms are ideally arranged in a cubic-close-packed fashion to form a negatively charged anion array comprised of face-sharing and edge-sharing X tetrahedra and octahedra. In the formula $A[B_2]X_4$, the A cations and B cations occupy tetrahedral and octahedral sites respectively. In the ideal spinel structure, with the origin of the unit cell at the centre ($\bar{3}m$), the close-packed anions are located at the 32e positions of the space group Fd3m. Each unit cell contains 64 tetrahedral interstices situated at three crystallographically non-equivalent positions 8a, 8b and 48f, and 32 octahedral interstices situated at the crystallographically non-equivalent positions 16c and 16d.

In the $A[B_2]X_4$ spinel, the A cations reside in the 8a tetrahedral interstices and the B cations in the 16d octahedral interstices. There are thus 56 empty tetrahedral and 16 empty octahedral sites per cubic unit cell.

The framework structure of the lithium metal oxide compound of the anode thus has, as its basic structural unit, a unit of the formula $[B_2]X_4^{n-}$ as hereinbefore described.

In the anode of the cell of the present invention, therefore, the B cations of the $[B_2]X_4^{n-}$ host framework structure may be regarded as being located at the 16d octahedral positions, and the X anions as being located at the 32e positions of the spinel structure. The tetrahedra defined by the 8a, 8b and 48f positions and the octahedra defined by the 16c positions of the spinel structure thus form the interstitial space of the $[B_2]X_4^{n-}$ framework structure for the diffusion of mobile Li^+ cations.

The B cations of the framework structure may consist of one cationic type, or more than one cationic type of identical or mixed valence to provide various $[B_2]X_4^{n-}$ framework structures, the overall charge of which can vary over a wide range.

Spinel compounds having the $[B_2]X_4^{n-}$ framework structure may also be characterized by crystallographic space groups other than the prototypic cubic space group Fd3m, and may therefore not have the ideal cubic-close-packed structures hereinbefore described. For example, in $Li_{1+x}[Mn_2]O_4$ compounds with $0<x<1$, ie compounds in

which A is Li, and B is Mn, the spinel structure is distorted, as a result of the Jahn-Teller Mn^{3+} octahedral site ions, to tetragonal symmetry, and the compound is characterized by the tetragonal space groups $F4_1/ddm$, or, alternatively, $I4_1/amd$ in which the tetrahedral and octahedral site nomenclature differs from that as defined by the space group Fd3m.

Furthermore, the anode need not necessarily be a stoichiometric spinel compound, but can instead be a defect spinel. Defect spinels are well known in the large family of spinel compounds and can have vacancies on the A sites, or on the B sites, or on both the A sites and B sites. For example, compounds can be synthesized in which defects are created by varying the quantity of B cations in the framework structure such that additional Li^+ cations can enter and leave the framework. In these instances additional Li^+ cations can partially occupy the 16d octahedral sites normally occupied by the B-type cations. Under such circumstances these partially occupied octahedra can be considered to form part of the interstitial space. Conversely, compounds can also be synthesized, in which part of the interstitial space defined by the 8a, 8b and 48f tetrahedral and 16c octahedral interstices of the spinel structure can be occupied by B-type cations, thereby rendering these particular sites at least partially inaccessible to the mobile Li cations. The $[B_2]X_4^{n-}$ framework structure can contain in certain instances a minor proportion, typically less than 10 atomic percent, of cations other than the mobile Li-type cations, or the A and B-type cations, within the framework structure or within the

interstitial spaces of the framework structure, and that could serve to stabilize the structure. For example, doped spinels of stoichiometry $Li_{1+\delta}Mn_{2-\delta}O_4$ where $0<\delta\leq0,1$, for example, $Li_{1,03}Mn_{1,97}O_4$ in which $\delta=0,03$, and $LiM_{\delta/2}Mn_{2-\delta}O_4$ where M=Mg or Zn and $0<\delta\leq0,05$, for example, $LiMg_{0,025}Mn_{1,95}O_4$, are more stable to cycling than the stoichiometric spinel $LiMn_2O_4$.

The compound of the anode may be a stoichiometric spinel selected from the group comprising $Li_4Mn_5O_{12}$, which can be written as $(Li)_{8a}[Li_{0,33}Mn_{1,67}]_{16d}O_4$ in ideal spinel notation; $Li_4Ti_5O_{12}$, which can be written as $(Li)_{8a}[Li_{0,33}Ti_{1,67}]_{16d}O_4$ in ideal spinel notation; $LiTi_2O_4$ which can be written as $(Li)_{8a}[Ti_2]_{16d}O_4$ in ideal spinel notation; LiV_2O_4, which can be written as $(Li)_{8a}[V_2]_{16d}O_4$ in ideal spinel notation; and $LiFe_5O_8$, which can be written as $(Fe)_{8a}[Fe_{1,5}Li_{0,5}]_{16d}O_4$ in ideal spinel notation.

Instead, the compound of the anode may be a defect spinel selected from the group comprising $Li_2Mn_4O_9$, which can be written as $(Li_{0,89}\square_{0,11})_{8a}[Mn_{1,78}\square_{0,22}]_{16d}O_4$ in spinel notation; and $Li_2Ti_3O_7$, which can be written as $(Li_{0,85}\square_{0,15})_{8a}[Ti_{1,71}Li_{0,29}]_{16d}O_4$ in spinel notation. In defect spinels, the distribution of Li^+ on the A and B sites can vary from compound to compound.

Instead, the compound of the anode may have a spinel-type structure, which can be a stoichiometric or defect spinel, with a mixture of transition metal cations such as a lithium-iron-titanium oxide in which the lithium and iron cations

are located on the A-sites, and lithium, iron and titanium cations on the B-sites.

In a preferred embodiment of the invention, the transition metal cations, Ti, V, Mn, Fe and Co, reside predominantly or completely on the B-sites of the spinel structure, while the Li cations reside predominantly or completely on the A-sites of the structure.

The lithium metal oxide compound of the cathode may also have a spinel-type framework structure. Thus, the framework structure of the lithium metal oxide compound of the cathode may then also have, as its basic structural unit, a unit of the formula $[B_2]X_4^{n-}$ of an $A[B_2]X_4$ spinel, as hereinbefore described, with the transition metal cations of the anode being more electropositive than those of the cathode.

In the compound of the cathode, A and B may be a metal cation of one type, or a mixture of different metal cations. The compound of the cathode may be a stoichiometric or defect spinel compound, as hereinbefore described.

When the compound of the cathode has a spinel-type structure, it may be selected from the group having as its B-type cations Li, Mn, Co or Ni, or mixtures thereof, such as $Li_xMn_2O_4$ where $0<x\leq1$ and $Li_xCo_2O_4$ where $0<x\leq2$, optionally doped with additional metal cations to stabilize the structure as hereinbefore described.

Instead, the compound of the cathode may have another structure type, for example a layered type structure such as that found within a system defined by a formula $Li_xCo_{1-y}Ni_yO_2$ where $0 \leq y \leq 1$ and $0 < x \leq 1$.

In general, the anode compound will be selected from those spinel compounds that offer a relatively low voltage vs pure lithium, typically those that offer 3V or less, while the cathode compound will be selected from those spinel compounds that offer a relatively high voltage vs pure lithium, typically those that offer between 4,5V and 3V. For example, a $Li/Li_{4+x}Ti_5O_{12}$ cell delivers on discharge at $100 \mu A/cm^2$ (for $0<x<1$) an average voltage of approximately 1,5V, while a $Li/Li_xMn_2O_4$ cell delivers on discharge at $100 \mu A/cm^2$ (for $0<x<1$) an average voltage of approximately 4V. Therefore, a cell in accordance with the invention can have $Li_{4+x}Ti_5O_{12}$ as an anode and $Li_xMn_2O_4$ as a cathode, and will deliver approximately 2,5V on discharge and which is approximately twice the voltage of a nickel-cadmium cell. In another example, a $Li/Li_2Mn_4O_9$ cell delivers a voltage of approximately 2,8V over most of the discharge. Thus, a cell in accordance with the invention can have a $Li_{2+x}Mn_4O_9$ anode and $Li_xMn_2O_4$ as cathode, and delivers approximately 1,2V on discharge, which is the typical voltage of a nickel-cadmium cell. It is convenient to load such cells in a discharged state, ie with the following configurations:

$Li_4Ti_5O_{12}$/Electrolyte/$LiMn_2O_4$ ....(1)

$Li_2Mn_4O_9$/Electrolyte/$LiMn_2O_4$ ....(2)

Although it is convenient to load such cells in a discharged state, the cells may also be loaded in the charged state, if so desired. In this respect, the anodes of the invention have lithiated spinel structures and delithiated spinel structures that have the $[B_2]X_4$ spinel framework as defined hereinbefore.

In (1), Li^+ ions are extracted from $Li[Mn_2]O_4$ during charge with a concomitant oxidation of the manganese ions from an average valence of 3,5 to higher values, and inserted into the $Li_4Ti_5O_{12}$ electrode structure with a concomitant reduction of the titanium cations from the average valence state of +4 to lower values. During this process Li^+ ions are shuttled between the oxide structures without the formation of any metallic lithium, the cell voltage being derived from changes in the oxidation state of the transition metal cations in the anode and cathode structures.

The electrolyte may be a room temperature electrolyte such as $LiClO_4$, $LiBF_4$, or $LiPF_6$ dissolved in an appropriate organic salt such as propylene carbonate, ethylene carbonate, dimethyl carbonate, dimethoxyethane, or appropriate mixtures thereof. Instead, however, it may be any appropriate polymeric electrolyte such as polyethylene oxide (PEO) - $LiClO_4$, PEO - $LiSO_3CF_3$ and PEO - $LiN(CF_3SO_2)_2$, that operates at room temperature or at elevated temperature, eg at about 120°C.

The invention will now be described by way of non-limiting examples, and with reference to the accompanying drawings in which:

FIGURE 1 shows powder X-ray diffraction patterns of compounds suitable for use as anode materials in rechargeable electrochemical cells according to the invention;

FIGURE 2 shows powder X-ray diffraction patterns of compounds suitable for use as cathode materials in rechargeable electrochemical cells according to the invention;

FIGURE 3 shows a plot of voltage vs capacity for a known $Li/Li_2Mn_4O_9$ cell;

FIGURE 4 shows a plot of voltage vs capacity for a known $Li/Li_4Mn_5O_{12}$ cell;

FIGURE 5 shows a plot of voltage vs capacity for a known $Li/Li_4Ti_5O_{12}$ cell;

FIGURE 6 shows a plot of voltage vs capacity for a known $Li/LiFe_5O_8$ cell;

FIGURE 7 shows a plot of voltage vs capacity for a Li/Li-Fe-Ti oxide cell;

FIGURE 8 shows a plot of voltage vs capacity for a known $Li/LiMn_2O_4$ cell;

FIGURE 9 shows a plot of voltage vs capacity for a known $Li/Li_{1.03}Mn_{1.97}O_4$ cell;

FIGURE 10 shows a plot of voltage vs capacity for a known $Li/LiCoO_2$ cell;

FIGURE 11 shows a plot of voltage vs capacity for the cell of Example 1 and which is in accordance with the invention;

FIGURE 12 shows a plot of voltage vs capacity for the cell of Example 2 and which is in accordance with the invention;

FIGURE 13 shows a plot of voltage vs capacity for the cell of Example 3 and which is in accordance with the invention;

FIGURE 14 shows a plot of voltage vs capacity for the cell of Example 4 and which is in accordance with the invention;

FIGURE 15 shows plots of voltage vs capacity for the cells of Examples 5 and 6 and which are in accordance with the invention; and

FIGURE 16 shows a cyclic voltammogram of the Li/Li-Fe-Ti oxide spinel cell of Example 7.

The following stoichiometric spinel and defect spinel compounds were selected for use as anode materials in the examples following hereinafter:

a) $Li_2Mn_4O_9$

b) $Li_4Mn_5O_{12}$

c) $Li_4Ti_5O_{12}$

d) $LiFe_5O_8$

e) Li-Fe-Ti oxide spinel in which Li:Fe:Ti=2:2:1

Powder X-ray diffraction patterns of these compounds are given in Figure 1a-e respectively.

The following spinel and non-spinel compounds were selected for use as cathode materials in the examples following hereinafter:

a) $LiMn_2O_4$ (spinel-type structure)

b) $Li_{1.03}Mn_{1.97}O_4$ (spinel-type structure)

c) $LiCoO_2$ (layered-type structure)

Powder X-ray diffraction patterns of these compounds are given in Figure 2a-c respectively.

EXAMPLE 1

In view thereof that a $Li/Li_2Mn_4O_9$ cell delivers on discharge 150mAh/g at an average voltage of approximately 2,8V, as indicated in Figure 3, and a $Li/LiMn_2O_4$ cell delivers on discharge 120mAh/g at an average voltage of approximately 3,8V, as indicated in Figure 8, a cell in accordance with the invention and having the configuration $Li_2Mn_4O_9$(anode)/Electrolyte/$LiMn_2O_4$(cathode) (2) was constructed.

The $LiMn_2O_4$ spinel compound of the cathode was synthesized by reaction of LiOH and γ-MnO_2 (chemically-prepared manganese dioxide, CMD) firstly at 450°C for 48 hours and thereafter at 750°C for 48 hours. The powder X-ray diffraction pattern of this compound is shown in Figure 2a.

$Li_2Mn_4O_9$ was synthesized by reaction of LiOH and $MnCO_3$ at 345°C for 32 hours. The powder X-ray diffraction pattern of this compound is shown in Figure 1a. The pattern is predominantly characteristic of the $Li_2Mn_4O_9$ defect spinel phase, but contains in addition a few very weak peaks, for example at 42°2θ and 53°2θ, that are indicative of a very minor proportion of lithiated γ-MnO_2 phase.

A cell of the format $Li_2Mn_4O_9$/Electrolyte/$LiMn_2O_4$ (2) was then constructed. The electrolyte used was 1M $LiClO_4$ in propylene

carbonate. The first 9 charge and 8 discharge cycles of the cell are shown in Figure 11. A current of 0,1mA was employed for both charge and discharge. The cell was cycled between upper and lower voltage limits of 1,5V and 0,45V respectively.

EXAMPLE 2

In view thereof that a $Li/Li_4Mn_5O_{12}$ cell delivers on discharge 150mAh/g at an average voltage of approximately 2,7V, as indicated in Figure 4, and a $Li/Li_{1,03}Mn_{1,97}O_4$ cell delivers on discharge 100mAh/g at an average voltage of approximately 3,9V, as indicated in Figure 9, a cell in accordance with the invention and having the configuration $Li_4Mn_5O_{12}$/Electrolyte/ $Li_{1,03}Mn_{1,97}O_4$ (3) was constructed.

The $Li_{1,03}Mn_{1,97}O_4$ spinel compound of the cathode was synthesized by the reaction of LiOH and γ-MnO_2 (chemically-prepared manganese dioxide, CMD) firstly at 450°C for 48 hours and thereafter at 650°C for 48 hours. The powder X-ray diffraction pattern of this compound is shown in Figure 2b.

$Li_4Mn_5O_{12}$ was synthesized by the reaction of Li_2CO_3 and $MnCO_3$ at 400°C for 10 hours. The powder X-ray diffraction pattern of this compound is shown in Figure 1b. The pattern is predominantly characteristic of the $Li_4Mn_5O_{12}$ spinel phase.

A cell of the format $Li_4Mn_5O_{12}$/Electrolyte/$Li_{1,03}Mn_{1,97}O_4$ (3) was then constructed. The electrolyte used was 1M $LiClO_4$ in propylene carbonate. The first 5 charge/discharge cycles of the cell are

shown in Figure 12. A current of 0,1mA was employed for both charge and discharge. The cell was cycled between upper and lower voltage limits of 1,6V and 0,5V respectively.

EXAMPLE 3

In view thereof that a $Li/Li_4Ti_5O_{12}$ cell delivers on discharge 120mAh/g at an average voltage of approximately 1,5V, as indicated in Figure 5, and a $Li/Li_{1,03}Mn_{1,97}O_4$ cell delivers on discharge 100mAh/g at an average voltage of approximately 3,9V, as indicated in Figure 9, a cell in accordance with the invention and having the configuration $Li_4Ti_5O_{12}$/Electrolyte/ $Li_{1,03}Mn_{1,97}O_4$ (4) was constructed.

The $Li_{1,03}Mn_{1,97}O_4$ spinel compound of the cathode was synthesized as in Example 2.

$Li_4Ti_5O_{12}$ was synthesized by the reaction of Li_2CO_3 and TiO_2, using a Li/Ti atomic ratio of 0,87, at 500°C for 12 hours and at 1000°C for 24 hours. A slight excess of lithium was used because of the volatility of Li_2O at that temperature. The powder X-ray diffraction pattern of this compound is shown in Figure 1c. The pattern is predominantly characteristic of the $Li_4Ti_5O_{12}$ spinel phase.

A cell of the format $Li_4Ti_5O_{12}$/Electrolyte/$Li_{1,03}Mn_{1,97}O_4$ (4) was then constructed. The electrolyte used was 1M $LiClO_4$ in propylene carbonate. The first 7 charge/discharge cycles of the cell are shown in Figure 13. A current of 0,1mA was employed for both

charge and discharge. The cell was cycled between upper and lower voltage limits of 2,8V and 1,9V respectively.

EXAMPLE 4

In view thereof that a $Li/Li_4Ti_5O_{12}$ cell delivers on discharge 120mA.Hrs/g at an average voltage of approximately 1,5V, as indicated in Figure 5, and a $Li/LiCoO_2$ cell delivers on discharge 140mA.Hrs/g at an average voltage of approximately 3,9V, as indicated in Figure 10, a cell in accordance with the invention and having the configuration $Li_4Ti_5O_{12}$/Electrolyte/$LiCoO_2$ (5) was constructed.

The $LiCoO_2$ spinel compound of the cathode was synthesized by the reaction of $CoCO_3$ and Li_2CO_3 firstly at 400°C for 48 hours and thereafter at 900°C for 48 hours. The powder X-ray diffraction pattern of this compound is shown in Figure 2c.

$Li_4Ti_5O_{12}$ synthesized as in Example 3, was used for the anode in this example.

A cell of the format $Li_4Ti_5O_{12}$/Electrolyte/$LiCoO_2$ (5) was then constructed. The electrolyte used was 1M $LiCoO_4$ in propylene carbonate. The first 3 charge/discharge cycles of the cell are shown in Figure 14. A current of 0,1mA was employed for both charge and discharge. The cell was cycled between upper and lower voltage limits of 2,8V and 1,9V respectively.

EXAMPLE 5

In view thereof that a $Li/LiFe_5O_8$ cell delivers on discharge 100mAh/g at an average voltage of approximately 1,0V, as indicated in Figure 6, and a $Li/Li_{1.05}Mn_{1,97}O_4$ cell delivers on discharge 100mAh/g at an average voltage of approximately 3,9V, as indicated in Figure 9, a cell in accordance with the invention and having the configuration $LiFe_5O_8$/Electrolyte/$Li_{1,03}Mn_{1,97}O_4$ (6) was constructed.

The $Li_{1,03}Mn_{1,97}O_4$ spinel compound of the cathode was synthesized as in Example 2.

$LiFe_5O_8$ was synthesized by reacting of Li_2CO_3 and α-Fe_2O_3 in a 1:5 molar ratio at 900°C for 24 hours. The powder X-ray diffraction pattern of this compound is shown in Figure 1d.

A cell of the format $LiFe_5O_8$/Electrolyte/$Li_{1,03}Mn_{1,97}O_4$ (6) was then constructed. The electrolyte used was 1M $LiClO_4$ in propylene carbonate. The first charge cycle of the cell is shown in Figure 15a. A current of 0,1mA was employed for both charge and discharge. The cell had an upper voltage limit of 4,1V.

EXAMPLE 6

In view thereof that a Li/Li-Fe-Ti oxide spinel cell delivers on discharge 80mAh/g at an average voltage of approximately 0,6V, as indicated in Figure 7, and a $Li/Li_{1,03}Mn_{1,97}O_4$ cell delivers on discharge 100mAh/g at an average voltage of approximately 3,9V, as indicated in Figure 9, a cell in accordance with the invention

and having the configuration Li-Fe-Ti oxide spinel/Electrolyte/ $Li_{1,03}Mn_{1,97}O_4$ (7) was constructed.

The $Li_{1,03}Mn_{1,97}O_4$ spinel compound of the cathode was synthesized as in Example 2.

A Li-Fe-Ti oxide spinel was synthesized by the reaction of Li_2CO_3 and Fe_2TiO_5, using a Li:Fe:Ti atomic ratio of 2:2:1, at 500°C for 6 hours and at 900°C for 16 hours. The powder X-ray diffraction pattern of this compound is shown Figure 1e. The pattern is predominantly characteristic of a spinel-type phase.

A cell of the format Li-Fe-Ti oxide spinel/Electrolyte/$Li_{1,03}Mn_{1,97}O_4$ (7) was then constructed. The electrolyte used was 1M $LiClO_4$ in propylene carbonate. The first charge cycle of the cell is shown in Figure 15b. A current of 0,1mA was employed for both charge and discharge. The cell had an upper voltage limit of 4,4V.

EXAMPLE 7

A Li-Fe-Ti oxide spinel was synthesized by the reaction Li_2CO_3 and Fe_2TiO_3 using a Li:Fe:Ti atomic ratio of 1:2:1 at 500°C for 6 hours, and thereafter at 900°C for 16 hours. A cyclic voltammogram of a Li/Li-Fe-Ti oxide spinel cell with an electrolyte of 1M $LiCO_4$ in propylene carbonate is shown in Figure 16. It shows the rechargeable characteristics of the Li-Fe-Ti oxide spinel electrode, and in particular, the rechargeability of the Li insertion/extraction reaction that occurs at approximately 1,5V versus lithium.

Examples 5, 6 and 7 show, in particular, the potential of using spinel-type oxides containing iron as anodes because they provide a low voltage against lithium. Furthermore, the experimental data provided in the examples demonstrate the ability of transition metal oxides to provide an electrochemical couple for 'rocking chair' rechargeable lithium cells in which lithium ions are transported between the two transition metal oxide electrodes, the anode of which has a spinel-type structure, and which uses a liquid or polymeric electrolyte containing Li^+ ions. The electrochemical cells of the invention thus contain no metallic lithium anode, and are therefore inherently safer than lithium cells containing metallic lithium anodes and, indeed, lithium-carbon anodes. In particular, such cells have an added advantage of providing a more constant operating voltage than cells with carbon anodes. Although the cells of the invention are designed primarily for the use as rechargeable cells, they can also, as indicated hereinbefore, be utilized as primary cells, if desired.

Although the principles of this invention have been demonstrated by use of lithium-metal oxide compounds, the compounds of the electrodes, instead of being oxides, can be sulphides.